Evaluation of Experimental Procedures for the Determination of Spray Characteristics of Orchard Sprayers

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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ABSTRACT

This study was designed to evaluate the use of a non-toxic dye as a substitute for a pesticide in measurements of spray characteristics of orchard sprayers. Filter paper was used as a substrate to collect the spray. The targets were suspended between wooden structures in a circular geometry around the path of the sprayer. This setup can provide a measure of the radial distribution of the pesticide and an estimate of how much material is emitted above the canopy, where it is readily available for drift. Two different sprayers were used in these tests. One high-volume sprayer (135 gal/acre) and a reduced-volume sprayer (27 gal/acre); the latter was operated with and without electrostatic charge. The sampling and analysis procedures described in this report proved to be capable of measuring the output of these sprayers at various angles. In a second set of experiments, the high-volume sprayer was used with a mixture of dye and pesticide to establish that the dye distribution can be used as an indicator for the pesticide distribution. Even though the ratio of dye to pesticide deposited on filter papers varied by almost an order of magnitude between samples, the distributions of dye and pesticide, based on their mean values, were in excellent agreement. Thus, this study showed that a fluorescent dye can be used successfully as a surrogate for pesticides in the evaluation of orchard sprayers.

ACKNOWLEDGEMENTS

This study would not have been possible without the extensive help of Prof. Ken Giles and Bill Steinke from the Agricultural Engineering Department at UC Davis. They provided the plot, the sprayers and their considerable expertise. Many thanks to the EHAP field crew that, besides coming out to Davis so many times for the spray runs, also helped in the design and construction of the sampling structures. Special thanks also to Laurie Braun who did most of the dye extractions at the West Sacramento facility. We like to acknowledge the support of the chemists from the CDFA laboratory at Meadowview for the initial method development of the dye analysis and for their analysis of the pesticide samples. Thanks also to Bruce Johnson and Peter Stoddard for reviewing this report.

DISCLAIMER

The mentioning of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or an implied endorsement of such product.

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INTRODUCTION

Over the last decade, a number of articles have been published in the scientific literature about the spray deposition of charged and uncharged droplets from air blast sprayers. All these studies, however, are only concerned with the deposition efficiency on the plant surfaces; they do not consider the potential for environmental problems caused by the material not deposited.

Low-volume electrostatic sprayers are intended to deliver pesticides to their targets efficiently by producing small, charged particles in the spray and reducing the volume of carrier used. Shifting the size distribution towards smaller particles makes them more susceptible to transport off-target. And maintaining the label rate while reducing the volume of the formulation produces higher concentrations of pesticide in the droplets, compounding the consequences of any off-target drift.

To assess drift potential, one has to know how much material is emitted above the canopy where the pesticide is readily available for transport off-site. It is necessary to know the angular distribution of pesticide in the spray in order to estimate the fraction emitted above the canopy.

In this study, we tested an experimental setup designed to determine this angular concentration distribution. To minimize the handling of pesticides, we also evaluated a non-toxic fluorescent dye as a substitute for a pesticide.

The specific questions that this study addressed were:

- Does the chosen experimental setup provide reliable data from which an angular concentration distribution can be calculated?

- What are the critical design parameters in this setup that influence the measurement of the concentration distribution?

- What are the optimum operating conditions with respect to minimizing sample variability and maximizing the signal strength?

- Is the dye a good substitute for a pesticide in terms of giving the same concentration distribution?

MATERIAL AND METHODS

Experimental Setup

To assess the radial distribution of sprayed formulation, it seems suitable to use a sampling structure with concentric geometry because an airblast sprayer ejects the formulation radially outward. Angular concentrations were determined by sampling at three angles on each side equidistant from the center of the sprayer. Each angle represented a thirty degree section between the horizontal and vertical directions. These sample locations are marked in Figure 1 by the symbols 2L to 4L and 2R to 4R for the left and right positions, respectively. Because the center of the sprayer was about three feet off the ground, a fourth sample was collected at a height of about two feet, measuring material emitted at this very low angle (locations 1L and 1R).

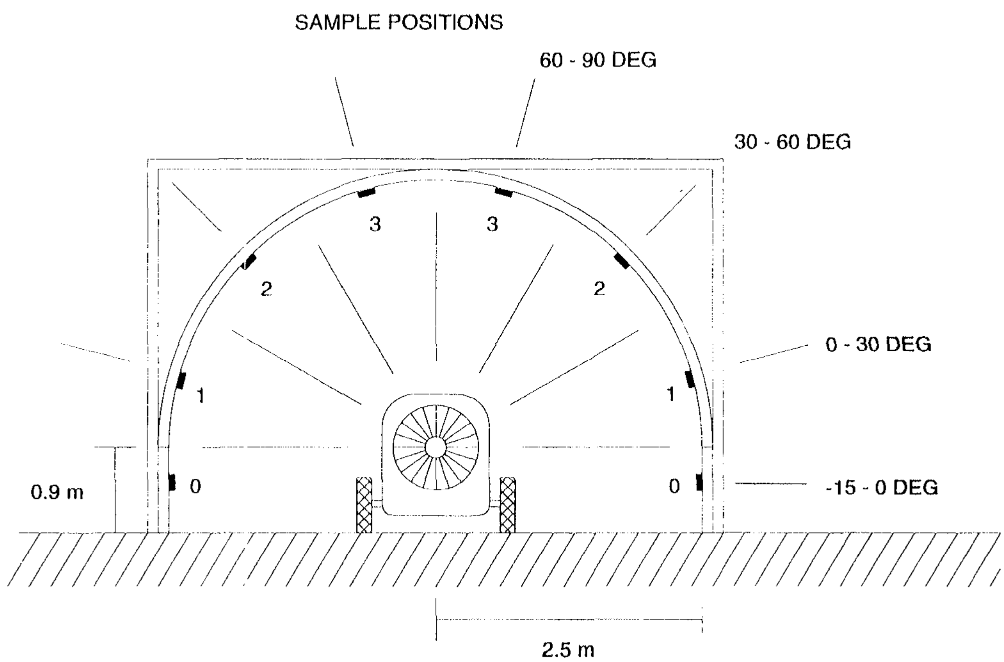

Figure 1 Cross-sectional view of sampling structure.

A wooden support structure was designed to hold the sampling material. To minimize the effects of air turbulence from the structure, the targets were suspended from thin nylon lines strung between two sampling structures about three meters apart (Figure 2). The targets were mounted near the center of each line to maximize the distance to the wooden supports.

The targets consisted of round pieces of filter paper in three diameters: 5.5, 7.0 and 9.0 cm. The analysis procedure, described in detail in Appendix A, measured the total amount of dye deposited on the filter paper. Because different sizes of paper were used, equal dye concentrations would yield lower total amounts for the smaller filter papers. Therefore, the number of filter papers put on the sampling structures was varied to keep the total surface area at about 250 cm^2: ten 5.5 cm targets were used, seven 7.0 cm targets and four 9.0 cm targets for each angle and side.

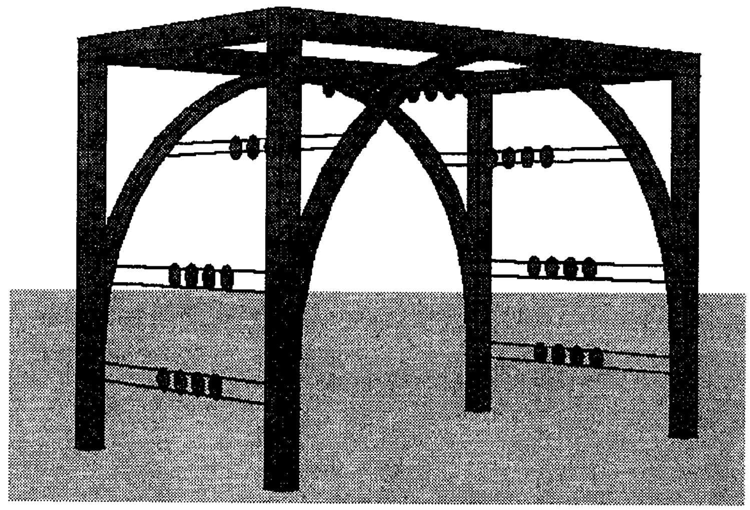

Figure 2 Sketch of sampling structure with filter paper targets.

We used both a loose and rigid way to mount the targets on the nylon lines (Figure 3). The loose method consisted of attaching the paper with one small plastic paper clip at the top to the upper line, so that the paper hung down vertically and was free to bend in the air flow, similar to a leaf. In the rigid method, the pieces of filter paper were clipped to a line at both the top and the bottom. In this case the paper stayed at a right angle to the direction toward the sprayer, unable to bend much even in the blast from a high-volume sprayer.

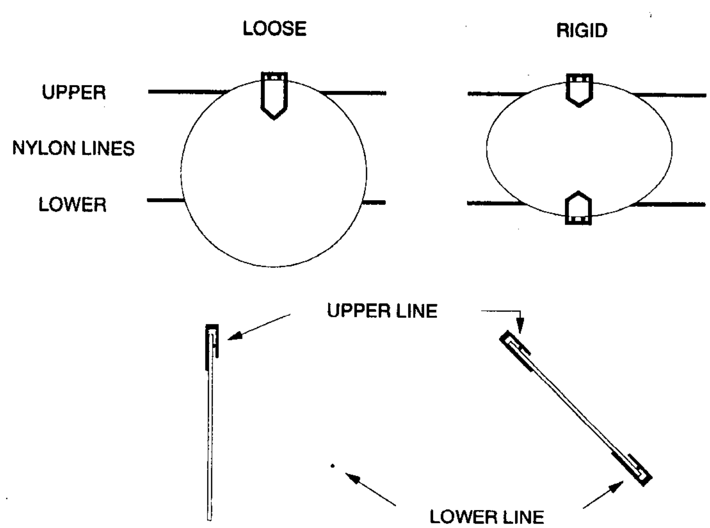

Figure 3 Loose and rigid mountings of filter paper targets.

All targets on a single structure were of the same size and mounting type. As there were six size-mounting combinations, six sampling structures were built in the field along a straight line with about ten meters distance between a set (Figure 4). The sprayer was driven through these six structures at a constant speed of about 3 km/h. The two samples at equal height left and right of the sprayer were combined in a single jar for a total of four samples per structure.

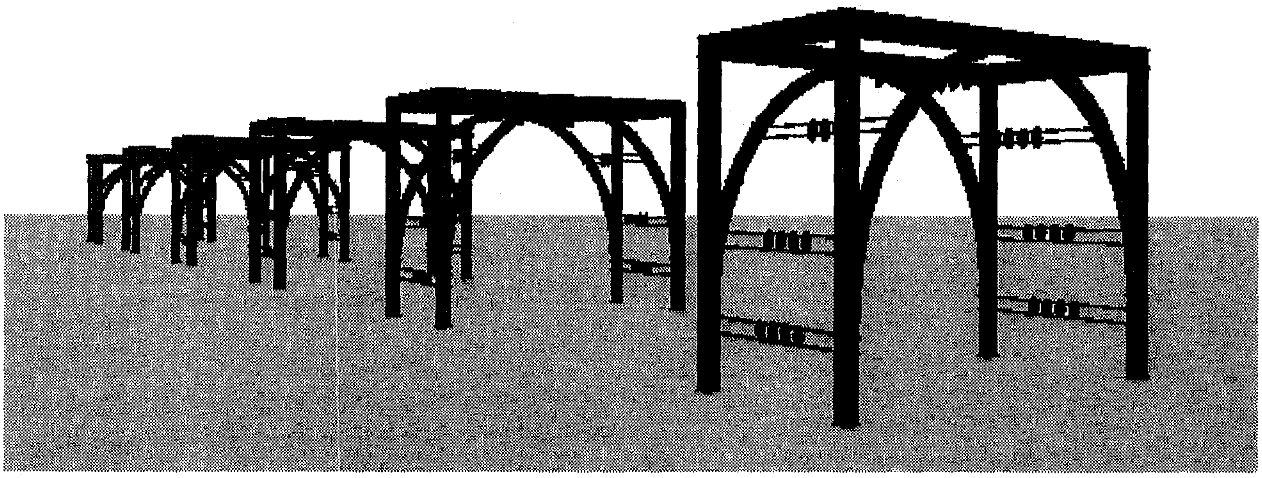

Figure 4 Row of six sampling structures.

Two different sprayers were used in the experiments: a high volume sprayer operating at 135 gal/acre, and a low volume sprayer set to 27 gal/acre. The low volume sprayer was run both with and without an electrostatic charge. The high volume sprayer was used in two different sets of runs: spraying dye only and spraying a dye/pesticide mixture. Captan was used as a representative pesticide to compare the behavior of the tracer to that of a pesticide formulation. Only the medium size papers were used as targets, mounted either loosely or rigidly on three structures each.

Because the dispersion of the spray emitted from the nozzles depended on meteorological conditions, wind speed, wind direction, temperature and relative humidity data were acquired before and during the experiments. Spraying was postponed when wind speeds exceeded 8 km/h.

Statistical analysis

The experimental design was a split-plot ANOVA with sprayer type as the main plot factor and the experimental treatments, mounting type and target size, as the subplot factors. Each pass of a sprayer through the six sampling structures constituted a main plot, while the sampling structures were the subplots within each pass. Sprayer passes were run in blocks of three, with one sprayer type randomly assigned to each pass. There were four dependent variables of interest: the concentrations of dye found on the targets in each of the four directions.

Under this analysis method, the incorporation of the continuous variables Wind, Wind Direction, Temperature and Relative Humidity would have been difficult. In addition, the first three runs were eliminated because of lab problems (Appendix A) and four additional data points were missing which necessitated an unbalanced ANOVA. The location of the sampling targets relative to the sprayer was a continuous measure with the dye being ejected radially outward. The sample targets were attached to a frame with distinct sides but the underlying measure is continuous. It is assumed that the amount of dye deposited in any direction changed in a smooth manner if the locations were moved in small increments. The target size was also a continuous measure and was easily included in the regression context. Sprayer type and mounting type were included through the use of dummy variables.

Differences in distribution of dye over the angles between mounting types and spray types were tested using interaction terms with the dummy variables. For this analysis, regressions were fit with dummy variables for the factor of interest and the interactions of the factor and the independent variable were included by multiplication. This is the equivalent of fitting the regressions separately to the levels of the factor, but with the ability to test for differences in response. The second step was to fit the same model to both groups combined. The significance of the improvement by allowing for different regressions at the different levels was then tested by the extra sum of squares test. For example, to test for a difference in distribution of dye over angle between loose and rigid mounting types, a regression model containing the dummy variable for mounting type and its interactions was fitted (the full model) and a model of dye only on angle was fitted (the reduced model). The extra sum of squares due to the inclusion of separate lines for each mounting type in the model was then found by subtraction. Details of the statistical analysis are provided in Appendix C.

Experimental Procedure

The tracer used in all experiments was a non-toxic, red fluorescent dye (Pylam Products Company, Acid Yellow 73). Suspensions of the dye in water were prepared the day before a treatment was scheduled. A captan formulation was used in the runs that required a pesticide/dye mixture (Captan 50-W, FMC Corporation). The tank concentration was approximately 4 lbs formulation per 100 gal water.

When the meteorological conditions looked favorable (i.e., wind speeds were expected to be below 8 km/h), one set of filter papers was placed on one sampling structure at the lowest angle as a background check. The filters were collected after 15 min, and the structures were then loaded with the filter paper targets according to the schedule printed in Appendix B.

In the meantime, the dye suspension was transferred to the sprayer tank and diluted with water to reach a concentration of 800 μg/L for the low-volume sprayer and 130 μg/L for the high-volume sprayer. The concentrations were varied according to the estimated flow rates for the sprayers so that the expected amounts of dye on the targets were roughly equal. The sprayer was then driven through the structures at a speed of about 3 km/h. Right after shutting off the sprayer, a tank sample was taken from the residual liquid dripping out of the nozzles. The filter papers were collected from the sampling structures and transferred to pint-size mason jars. During storage, the jars were kept in the dark at room temperature.

The dye was then extracted from the filter paper in a sonicator using methanol as a solvent. The dye concentration in the solution was determined using a scanning spectrofluorophotometer (Shimadzu RF-450). In the case of the dye/pesticide mixture, a few milliliters of the extract were used for the dye analysis, the remainder for the pesticide analysis. A detailed description of the procedure is given in Appendix A.

RESULTS AND DISCUSSION

The analysis results for all dye and pesticide samples are listed in Appendix D. The major factors influencing the amount of dye deposited were: run number, sprayer type, target size, target mounting and target angle. Figure 5 shows some representative data for the five low volume sprays without charge. Plotted are the dye concentrations of the targets for the four sampling angles. The three columns at each angle represent the small, medium and large targets, respectively. Solid symbols are used for the loosely mounted targets, open symbols for the rigidly mounted ones. It is immediately apparent that there is a large variation between runs (for example, the loosely mounted, medium sized targets at angle two range from 0.48 to 1.34 $\mu g/cm^2$). No correlation has been found with any of the measured parameters that could explain this variability.

Though the absolute amount of dye deposited varied between runs, the relative distribution between the four angles was more consistent. As seen from Figure 6, size and mounting differences were not important in determining the fraction of dye deposited. The run to run variability, however, was reduced only by a small amount. In spite of this noise (indicated by the vertical spread of the data points in Figure 6), the average dye depositions for the different target types (represented by the lines in Figure 6) were very similar. This implies that there were no significant differences between the various sampling methods used in this study with respect to the relative dye distribution.

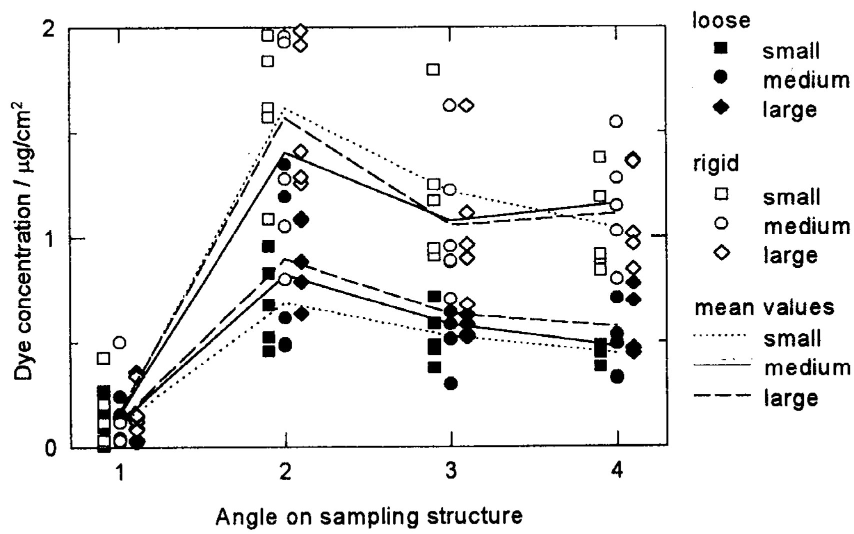

Figure 5 Dye concentrations at the four angles for the low volume sprays.

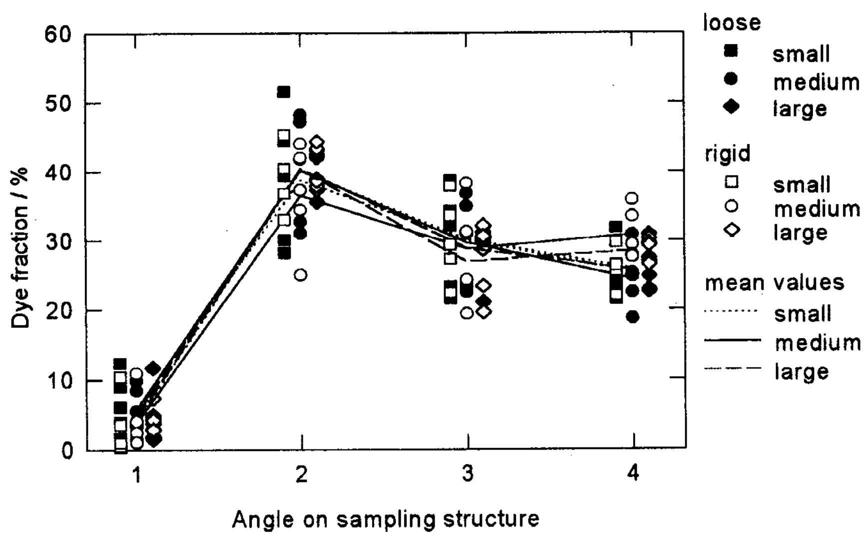

Figure 6 Distribution of the amount of dye deposited at the four angles for the low volume sprays.

For the absolute amounts of dye deposited, however, Figure 5 shows that there was a pronounced effect of the mounting type: rigidly mounted targets had a higher dye concentration than loosely mounted ones. The loose targets were flapping wildly in the turbulence from the air blast sprayers; the rigid ones were just bending a little bit due to some play in the supporting line. It is possible that the rigid ones were just bending a little bit due to some play in the supporting line. It is possible that because of this bending the loose targets had a smaller apparent cross section and thus accumulated less dye.

Table I summarizes the amounts of dye deposited on the targets and lists the ratio of the concentrations between the rigid and loose mounting. This ratio seems to be quite independent of the spray type, but increases for the higher angles. A possible explanation for this effect is that for the loosely mounted filters the apparent cross section varied with the sampling angle, whereas the rigid filters were always perpendicular to the direction towards the sprayer (Figure 3). Because of the varying cross section, the loosely mounted filters may have received a smaller total amount of dye resulting in a lower concentration.

Table I Comparison between loose and rigid mounting for the three spray types.

Angle	**Sprayer**	**Mount**	**Dye conc.(μg/cm²)**		**rigid/loose**
			mean	**stdev**	**ratio**
1	low	loose	0.12	0.1	
		rigid	0.16	0.15	1.4
	elec	loose	0.3	0.18	
		rigid	0.43	0.21	1.4
	high	loose	0.72	0.18	
		rigid	1.09	0.28	1.5
2	low	loose	0.8	0.28	
		rigid	1.53	0.39	1.9
	elec	loose	0.96	0.38	
		rigid	1.62	0.49	1.7
	high	loose	0.91	0.17	
		rigid	1.48	0.36	1.6
3	low	loose	0.58	0.16	
		rigid	1.12	0.34	1.9
	elec	loose	0.6	0.28	
		rigid	1.23	0.68	2.1
	high	loose	0.98	0.2	
		rigid	1.62	0.44	1.7
4	low	loose	0.5	0.13	
		rigid	1.1	0.23	2.2
	elec	loose	0.5	0.25	
		rigid	1.05	0.54	2.1
	high	loose	0.8	0.15	
		rigid	1.51	0.4	1.9

Figures 7 a) to c) present the mean dye deposition for the three spray types. The loosely mounted targets showed no significant difference between the three sizes. The rigidly mounted papers exhibited two anomalies: the large, rigid targets in the high volume spray runs had a significantly lower deposition than the small and medium ones, and the targets at angle three of the electrostatic spray showed a large separation for the three sizes.

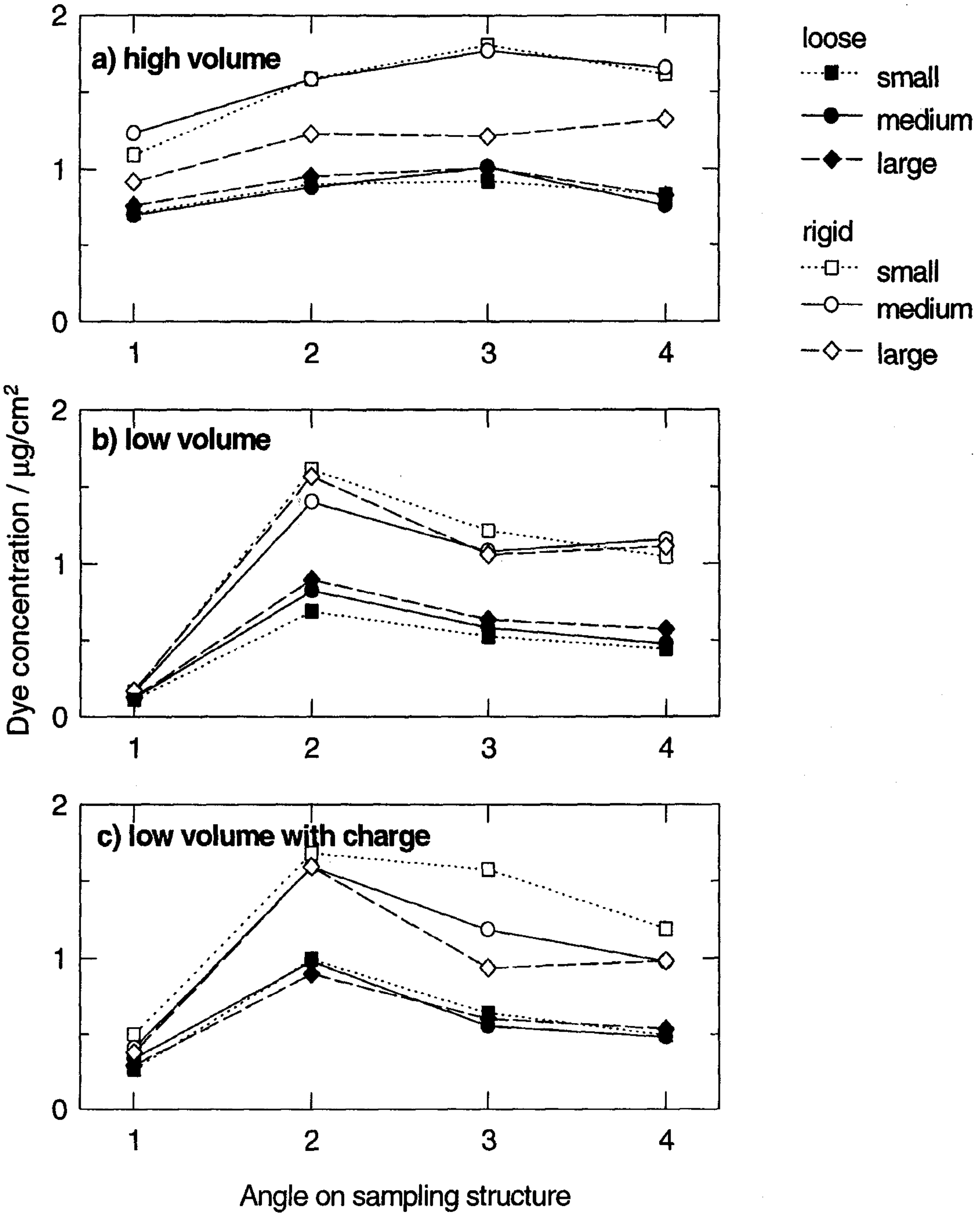

Figure 7 Mean dye deposition for the three spray types.

There was not much difference between the low volume sprays with and without charge, as can be seen from Table I and Figure 7. The main effect was a higher concentration at the lowest angle for the electrostatic spray. Also, for angles two to four, the standard deviations for the electrostatic spray were almost twice as high as the ones for the low volume spray without charge.

Four additional runs were done with the high volume sprayer about one month later using a captan/dye mixture. Only medium sized targets were used in this case. Figure 8 shows a comparison of the dye and captan concentrations. Despite a large scatter in the data, the agreement between the distribution of the dye and the distribution of the pesticide was very good. The close match of the mean values is more visible in Figure 9.

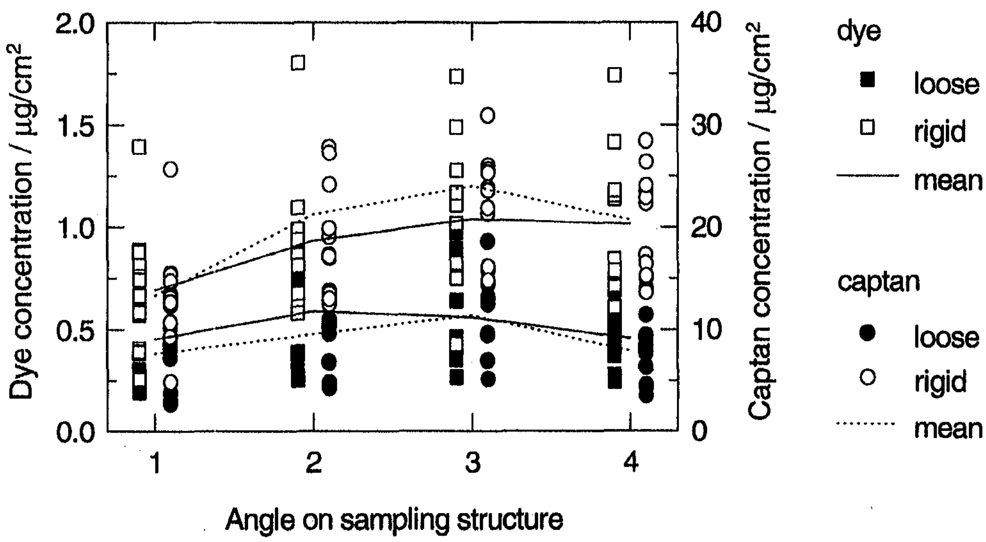

Figure 8 Dye and pesticide concentrations at the four sampling angles for loose and rigid target mountings.

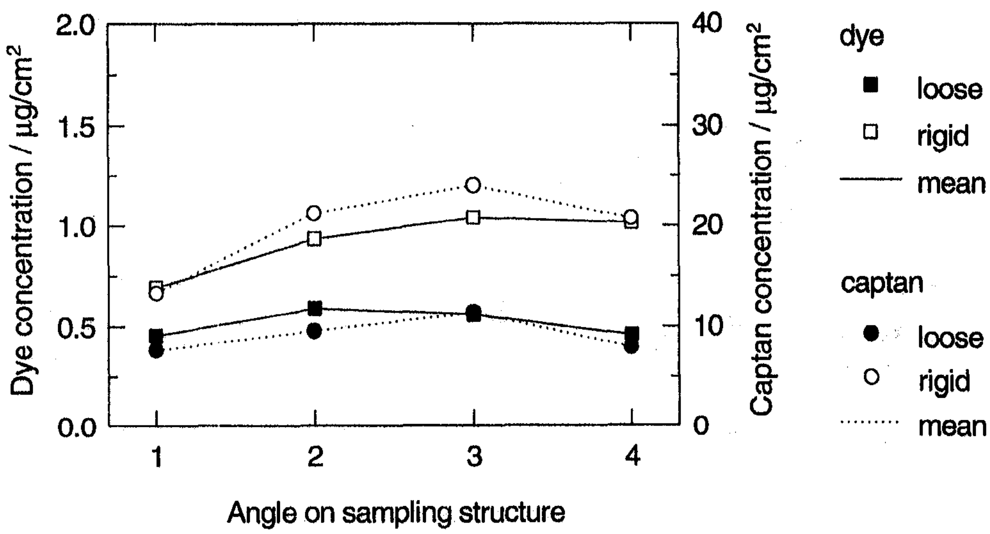

Figure 9 Mean dye and pesticide concentrations at the four sampling angles for loose and rigid mountings.

Fortuitously, the ratio of the mean captan and mean dye concentrations as analyzed from the filter paper targets was 20.2, which was very close to the mass ratio of 20 used in preparing the tank mixture. This close match, however, was the ratio of two averages from 92 samples. Actual captan/dye ratios ranged from 9.5 to 58.9 with a median of 16.7 and a mean of 21.7.

Table II compares the calculated output of the sprayers with the measured amounts found on the paper targets. The tank concentrations in g/gal were based on the measured amounts of chemical and water added to the spray tank. The flows were determined by measuring the time it took to spray a known amount of water. The output of dye and captan in g/min was based on the average sprayer speed of 5510 cm/min. Assuming that the spray was distributed over an 210° arc at a distance of 2.5 m from the center of the sprayer (Figure 1), one can calculate the average concentrations in μg/cm^2. The measured concentrations listed in the next two columns were derived by averaging the dye concentrations listed in Table I over the four angles. Recoveries were determined from the calcutated output and the measured deposition.

Table II Comparison of calculated sprayer output and measured deposition.

Sprayer	Compound	Tank g/gal	Flow gal/min	Output* g/min	Output* μg/cm^2	Measured μg/cm^2 loose	Measured μg/cm^2 rigid	Recovery % loose	Recovery % rigid
low	dye	3	2.48	7.44	1.47	0.50	0.98	34	66
low, elec	dye	3	2.48	7.44	1.47	0.59	1.08	40	74
high	dye	0.5	12.24	6.12	1.21	0.86	1.43	71	118
high	mix, dye	0.5	12.24	6.12	1.21	0.52	0.92	42	76
high	mix, captan	10	12.24	122.4	24.25	9.14	19.81	38	82

*) The output is based on a mean sprayer speed of 5510 cm/min and a length of 916 cm for the 210° arc covered by the sprayer (see Figure 1).

In general, this calculation yielded reasonable values for the recoveries, which indicates that, even with the coarse 30° target spacing used in this study, the measured distribution can account for the total sprayer output. Another result was that the rigid mounting method yielded higher recoveries. The recoveries for the high volume sprayer with dye only and the dye/captan mixture were quite different, but the numbers are not immediately comparable because the dye only targets were extracted by our group in West-Sacramento, while the dye/captan mixture was extracted by the chemistry laboratory in Meadowview. Among the dye-only runs, the high volume sprayer had a significantly higher deposition than the other two sprays, even though the dye concentration in the output of the high volume spray was lower by about 20%.

SUMMARY AND CONCLUSIONS

The statistical analysis of dye and pesticide concentrations showed that the angular distribution of the dye tracer was equivalent to that of the pesticide itself. However, the large scatter in the data indicated that too small a sample size might lead to incorrect results. Fortunately, the dye analysis was fast and inexpensive, making it feasible to collect a large number of samples.

Among the various mounting and size combinations tested, none of them seemed to affect the measured dye distribution significantly. In all cases, though, rigidly mounted targets collected more material than loosely mounted ones. That the ratio of the collection efficiency for loosely mounted and rigidly mounted targets changed with the position on the sampling structure indicated that there was a bias in the sampling setup in at least one of the cases. The statistical analysis showed that there was a curve in response over angle for the rigid mounting method but not for the loose mounting.

This study was designed to test the performance of the dye as a substitute for a pesticide, not to compare the performances of the sprayers. Thus, the following conclusions may not be applicable outside the context of this study. The only significant result regarding the sprayers was that the high volume sprayer had higher concentrations of dye deposited than either of the low volume sprays. There was no statistically significant difference between the low volume sprays with and without electrostatic charge in this study.

APPENDICES

A: Method development

General Procedure

The dye deposited on the filter paper is extracted with methanol and an aliquot of the extract is then analyzed. The dye concentration in the extract is determined from its fluorescence intensity based on calibration data. Some initial method development was performed by the chemistry laboratory at Meadowview. Their findings were:

- Methanol and acetone are suitable solvents.
- The optimum operating conditions of the spectrofluorometer are excitation at 480 nm with an emission peak near 550 nm.
- The peak height of the samples decayed rapidly during the first 15 min in the measurement cuvette before reaching a plateau.
- When the samples were filtered before transferring an aliquot into a cuvette, the signal was lower but showed no initial decay.
- The recovery of the dye from the filter paper is about 106%.
- The dye decays rapidly in sunlight with a halflife of about 6 hrs.

After the first two and a half sample sets were analyzed, problems with the spectrofluorometer at Meadowview became apparent. From then on, the analysis was performed using the instrument in the departmental laboratory of the Environmental Toxicology department at UC Davis. The sample extractions were done at the West Sacramento facility. Some additional method development was necessary because of the different results obtained with the more powerful instrument at Davis. The following sections describe the instrumental parameters for the analysis, the extraction procedure for the samples and other method development like calibration curve and recoveries of the dye from the filter paper substrate.

Sample Extraction

Outline:

- Take a sampling jar containing the exposed filters.
- Cut the filters into small pieces and return them into the jar.
- Put the jar onto a scale, weigh it and then zero the readout.
- Add 100 g of methanol.
- Sonicate for 15 min.

- Weigh the jar again.
- Transfer a 25 ml aliquot into a brown glass storage bottle using a syringe with a 0.45 μm filter.
- Label the bottle with the sample number and store it in a dark place.

Detailed procedure:

Each of the experimental runs should be treated as one set of samples which consists of 25 jars with filter papers: 1 field blank and 24 samples. Each set should be extracted together on a single day. The sets will be extracted in numerical sequence. The 24 field samples in a set are stored in 2 boxes of 12 jars each. The field blanks are stored in separate boxes. Divide this set into 6 subsets of 4 jars each. Sonicate the blank separately or with the spikes. This division is necessary because the sonication bath can handle only a limited number of jars. Do not put more than 4 jars in the sonicator or the efficiency of the ultrasound will be reduced.

Take a jar and cut the filters into small pieces of about one to two square inches size. Set the jar on a scale, record the weight and tare it to zero. Rinse the scissors with methanol into the jar then continue filling with methanol to 100 g. The actual amount of methanol is not that crucial because the dye concentration will be determined by weight at the end of this procedure. Repeat this step for the first four sample jars.

When the first four jars are ready, fit them in the frame on the sonicator. Tilt each jar as it is added to the bath to release any air bubbles from underneath. Fill the bath to within one inch or less from the surface of the sonicator and sonicate the jars for 15 min. Do not let the water level drop below the inch line while sonicating the samples. Also, do not set containers on the tank bottom; this dampens the sound energy and may cause damage to the sound transducer.

Put adhesive tape on four 30 ml brown glass storage bottles and write the corresponding sample numbers on the tape. Remove a sample jar from the sonicator, wipe of the moisture on the outside and weigh the jar again. The difference between the dry weight and this final weight is the amount of methanol added. Under the hood, rinse the bottle twice with a few milliliters of the sample extract, then transfer 25 ml of the sample to its corresponding brown bottle filtering it through a 0.45 μm syringe filter. Discard the remaining liquid into a waste container. Allow the filters to dry out under the hood then discard them into the garbage. Destroy the sampling jars. Continue processing the remaining samples the same way.

Notes:

The samples are light sensitive and are kept in boxes in the lab to prevent light exposure. It is alright to have them exposed to room light during the extraction, but samples should not be left out in the light for longer periods.

Each set of samples and the associated quality control samples require one gallon of methanol. Always start with a fresh one gallon bottle. Number these bottles consecutively and record in the log which bottles were used for a given set. Also, fill one 30 ml brown glass storage bottle with a methanol sample from each bottle and label it as BLANK #*n* where *n* is the number of the methanol bottle. Do not discard the leftover methanol as it is used to prepare some quality control samples.

Analysis Procedure

The fluorescence intensity of the dye was measured with a Shimadzu RF-540 scanning spectrofluorometer. The critical parameters that determine the signal intensity and the signal-to-noise ratio are the excitation and emission wavelengths. To identify the optimum combination of excitation and emission wavelengths, the fluorescence signal at 545 nm was scanned as a function of the excitation wavelength. There are two maxima in the fluorescence signal: a large maximum at 480 nm excitation and a small one at 340 nm excitation.

Figure 10 shows the emission scans for those two excitation wavelengths. The fluorescence intensity for the 480 nm excitation is a factor of five higher than for excitation at 340 nm. Thus, excitation at 480 nm translates into a five times lower detection limit. However, in this study the major limitation on the precision is not caused by random noise, but rather by the ability to quantitatively subtract the background. The large interference at 480 nm, caused by stray light from the excitation, makes it nearly impossible to perform a reliable background subtraction. All analyses were done using an excitation wavelength of 340 nm because the loss in sensitivity was more than compensated by the increased accuracy in the background subtraction.

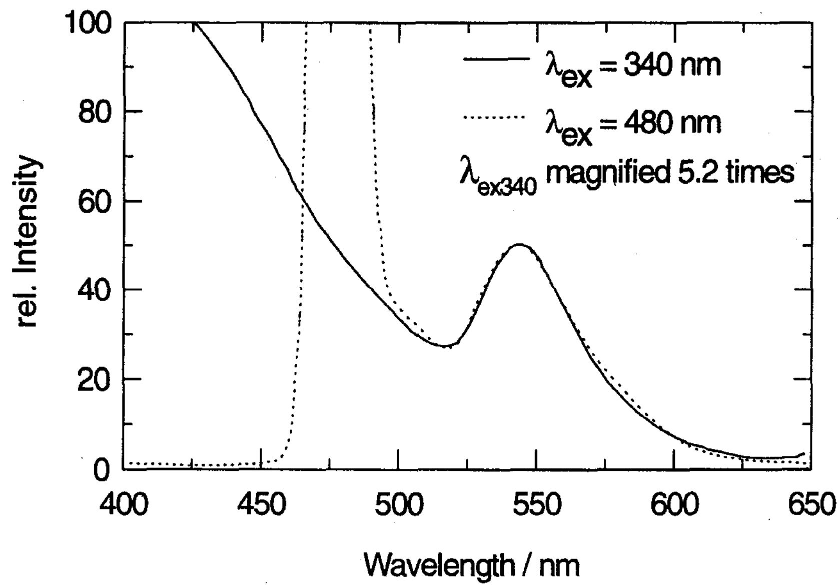

Figure 10 Fluorescence spectra for the two emission wavelengths of 340 nm and 480 nm. The trace for 340 nm excitation is magnified 5.2 times to allow better comparison of the shapes.

The settings for the Shimadzu RF-540 spectrofluorophotometer are listed in Table III. The stability and reproducibility of the measurements was high enough to use a fast scanning speed of about 100 nm/min. The acquisition time of one spectrum per three to four minutes allowed to analyze up to 100 samples per day. A few combinations of slit widths were checked, and a setting of 10 µm for both the excitation and the emission side yielded optimum results. Increasing the excitation slit width to 20 µm nearly quadrupled the signal but reduced the resolution by about 20%. Because the signal strength was good enough even with 10 µm slits, the slight loss in resolution was considered more important than the gain in signal strength.

Table III Settings of the Shimadzu RF-540 spectrofluorophotometer.

Abscissa scale:		3	(x4 magnification)
Ordinate scale:		depending on sample	
Scan speed:		2	(fast)
Excitation:		345.0 nm	
Emission:	1 =	470.0 nm	(start scan)
	2 =	630.0 nm	(end scan)
Slit width:	1 =	3	(10 µm)
	2 =	3	(10 µm)

The intensity of the background shown in Figure 10 varies from one spectrum to another and thus cannot be corrected by subtracting a constant value determined in a separate blank measurement. A simple linear interpolation of the baseline would also yield unsatisfactory results because of the pronounced curvature of the background. An additional complication arises from an elevated background in all samples that had come in contact with the filter paper used as the sampling substrate. In this case, the best approach to separate the dye signal from the background is to express the observed signal as a linear combination of three components: dye, paper and solvent (Figure 11).

One could use a least-squares fitting procedure of the three components to a sample spectrum according to:

$$\textit{minimize} \;\; (I_{\lambda sample} - I_{\lambda fit})^2 \;\; \textit{for}$$
$$I_{\lambda fit} = c_1 + a_1 * I_{\lambda solvent} + a_2 * I_{\lambda paper} + a_3 * I_{\lambda dye}$$

where I_λ refers to the intensity at a given wavelength. The fluorescence intensity of the dye in the unknown spectrum is then equal to a_3 times the intensity of the dye in the reference used for the fitting procedure. The spectra are digitized at 0.5 nm intervals, so about 300 data points are available for the regression calculation.

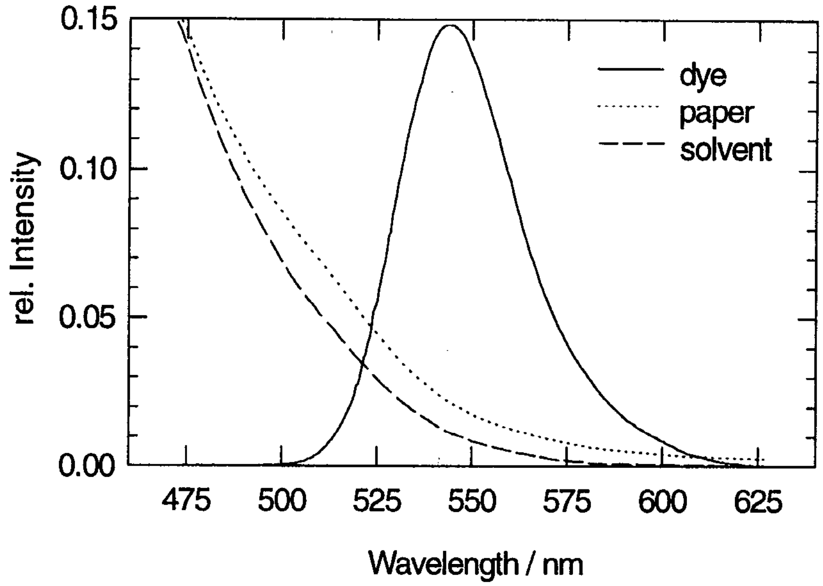

Figure 11 Fluorescence traces for the three components of a sample spectrum: dye, paper and solvent.

The drawback of this approach is that there is little visual feedback about how reasonable the fitting results are. For this reason, a stepwise approach is preferable. First fit just the two backgrounds (parameters a_1 and a_2), then subtract the fitted curve from the sample spectrum. The dye reference is then fitted to the residual:

$$STEP1:\ minimize\ (I_{\lambda_{sample}} - I_{\lambda_{fit1}})^2\ for$$
$$I_{\lambda_{fit1}} = c_1 + a_1 * I_{\lambda_{solvent}} + a_2 * I_{\lambda_{paper}}$$

$$STEP2:\ I_{\lambda_{residual}} = I_{\lambda_{sample}} - I_{\lambda_{fit1}}$$

$$STEP3:\ minimize\ (I_{\lambda_{residual}} - I_{\lambda_{fit2}})^2\ for$$
$$I_{\lambda_{fit2}} = c_2 + a_3 * I_{\lambda_{dye}}$$

For this approach to work, it is necessary to identify parts of the trace where the background is dominant and parts where the dye contributes to the shape. From Figure 11 it can be seen that the signal from the dye is limited to the wavelength range between about 510 nm and 615 nm. The wavelengths above and below this range can be used to fit the two backgrounds.

Plot A in Figure 12 shows that a fit of the solvent and paper background to the whole spectrum yields nonsense; after ignoring the wavelength range of the dye peak, however, the fit produces an excellent match to the background (plot B). Subtracting this fit from the spectrum produces the residual dye spectrum shown in plot C. A fit of the dye reference to this residual gives such a close match that the dotted curve is hardly visible in the figure.

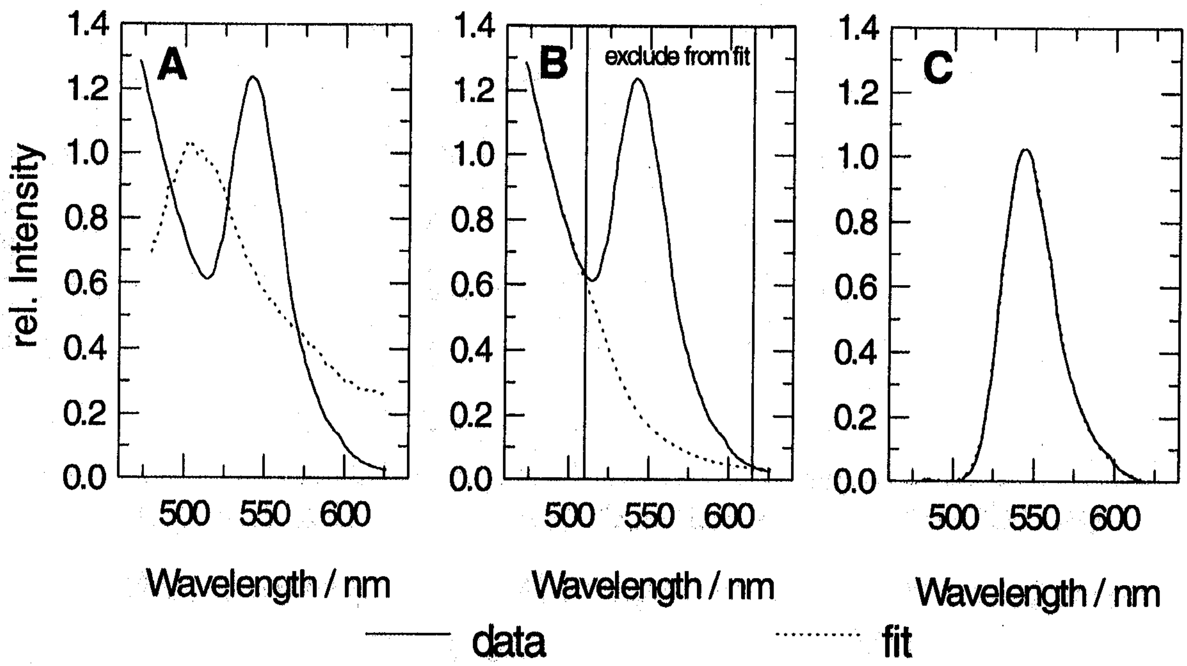

Figure 12 Fit to large signal: (A) background fitted to whole spectrum; (B) fit ignoring dye peak; (C) fit of dye reference to residual after background subtraction.

The power of this technique becomes apparent when the sample spectrum contains much less dye. Plot A in Figure 13 contains a sample spectrum that would have yielded a non-detect result if a conventional integrator or visual analysis had been used. When a background fit is overlayed onto that trace (plot B), a definite contribution from the dye component is becomes visible. Plot C shows the residual trace after background subtraction and the fitted dye reference spectrum.

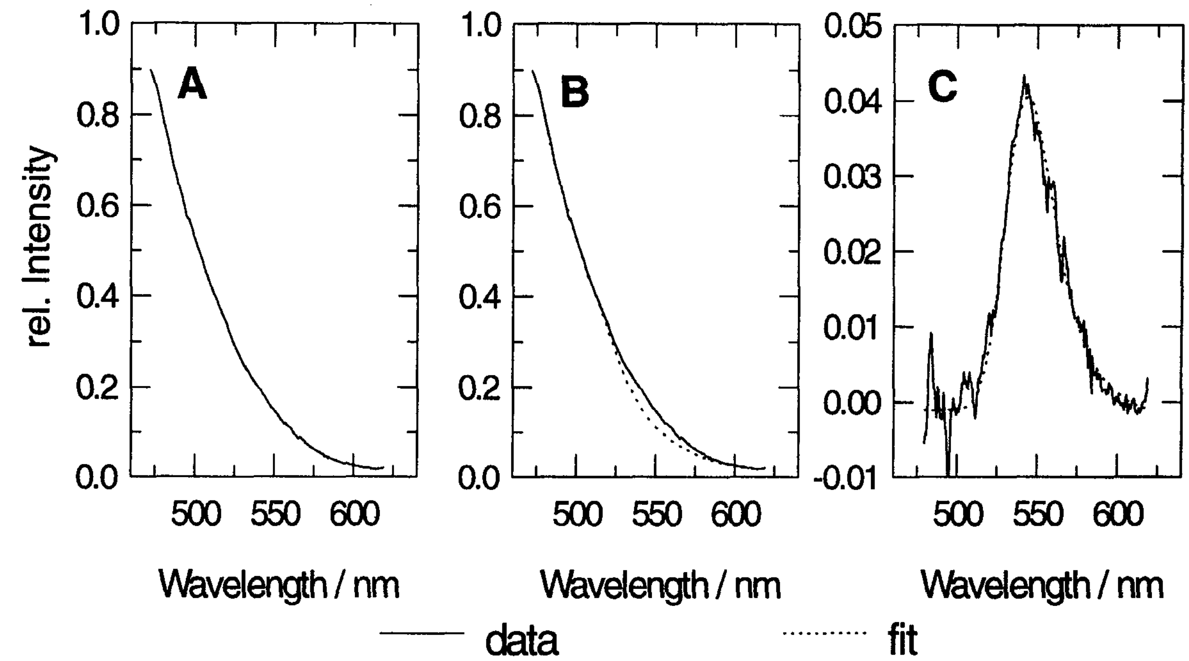

Figure 13 Fit to small signal: (A) sample; (B) background fit to sample; (C) dye reference fit to residual after background subtraction.

Calibration

The analysis procedure described above yields dye fluorescence intensities for each sample. These intensities are converted into a concentration using the following equation:

$$C_{dye} = \frac{(a_3 * I_{\lambda_{dye}} - f_0) * f_1 * V_{solvent}}{A_{filter}}$$

where C_{dye} is the dye concentration on the filter paper in µg/cm², $a_3 * I_{\lambda dye}$ the calculated intensity of the dye fluorescence signal, f_0 and f_1 the intercept and slope of the calibration curve, $V_{solvent}$ the volume of the extraction solvent and A_{filter} the total area of the filter papers in each sample. Four to five calibration points were analyzed with each sample set. All calibration data were combined (as shown in Figure 14), and the slope and intercept of the regression line were used as calibration factors for all data. The value for the intercept was f_0 = -0.004 with a standard deviation of 0.008, and the slope was 0.299 with a standard deviation of 0.003. The fit had a r-squared value of 0.995.

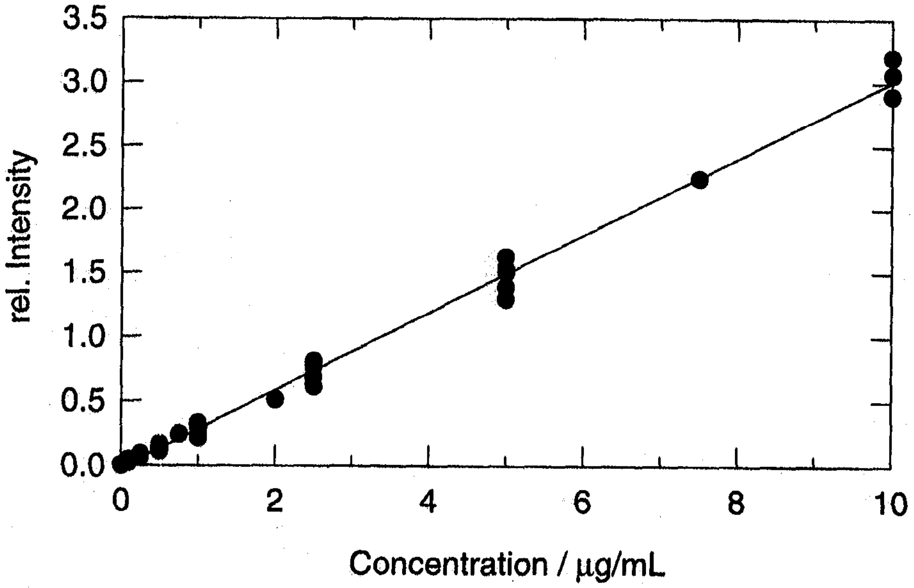

Figure 14 Calibration curve.

B: Experimental Layout

Run	Sprayer	Treatment for structure #					
		1	2	3	4	5	6
1	low, elec	1	6	4	3	2	5
2	low	1	2	3	4	5	6
3	high	3	1	4	6	2	5
4	low, elec	5	4	2	1	6	3
5	high	2	6	3	5	1	4
6	low	2	6	4	3	1	5
7	high	5	3	6	2	4	1
8	low	3	4	5	6	2	1
9	low, elec	3	2	6	5	4	1
10	low	4	1	6	5	3	2
11	low, elec	6	5	3	2	1	4
12	high	4	2	5	1	3	6
13	low, elec	4	3	1	6	5	2
14	low	5	3	1	2	6	4
15	high	1	5	2	4	6	3
16	low, elec	2	1	5	4	3	6
17	low	6	5	2	1	4	3
18	high	6	4	1	3	5	2

Treatments:

1 loose target mounting, small target size
2 loose target mounting, medium target size
3 loose target mounting, large target size
4 rigid target mounting, small target size
5 rigid target mounting, medium target size
6 rigid target mounting, large target size

C: Statistical Analysis

In the following text, all parameters being tested for significance were given α parameter labels while those not tested were designated by β's. In sequential tests parameters for variable coefficients may be designated by α's in the first test and β's in the second if they were not tested after the first test.

Tests of Distribution Between Dye and Captan

The first step was to test for differences in dye distribution against captan distribution to determine the adequacy of dye as a surrogate for pesticide. A log transformation was applied to the dye and captan data after combining because of the large difference in mean and variance between dye and captan. After transformation, the differences were reduced but an indicator variable was still required to compensate for the significant difference in mean. An indicator variable for mounting type was also required to account for the previously observed difference in deposition between loose and rigid mounts. The regressions for tests of dye against captan all included the chemical and mount dummy variables. Large differences in concentration of dye and captan were known to exist and differences in concentration between the mounting types were also found. In addition, a significant temperature correlation was found in a screening run. Therefore temperature was included in the regressions to reduce environmental differences between experimental runs.

Test For Difference in Distribution of Dye and Captan Over Angle Between Mount Types

Full Model: $\text{Concentration}=\beta0+\beta1(\text{Temperature})+\beta2(\text{Compound})+\beta3(\text{Mount})$
$+\beta4(\text{Angle})+\beta5(\text{Angle}^2)+\alpha1(\text{Mount*Angle})+\alpha2(\text{Mount*Angle}^2)$

Ho: The mounting types differ only in level. ($\alpha1$ and $\alpha2=0$)

Reduced Model: $\text{Dye}=\beta0+\beta1(\text{Temperature})+\beta2(\text{Compound})+\beta3(\text{Mount})$
$+\beta4(\text{Angle})+\beta5(\text{Angle}^2)$

The extra sum of squares for a1 and a2 is given by

SS(b1,b2,b3,b4,b5,a1,a2|b0) - SS(b1,b2,b3,b4,b5|b0)
= RegressionSS(Full Model) - RegressionSS(Reduced Model)
with 7-5=2 degrees of freedom.

F = (ESS/2)/MSE(Full Model) = (443.566-442.773)/2/.165 = 2.40 p>.05

Accept Ho: The mounting types differ only in level, not in distribution over angle. ($\alpha1$ and $\alpha2=0$)

Test For Difference in Distribution Over Angle Between Compounds

The next question was to see if there were significant differences in slope parameters between the dye and captan curves over angle. This test required a new full model with the Compound*Angle and Compound*Angle^2 interaction terms replacing the Mount interaction terms, which the previous test showed to be unnecessary.

Full Model: $\text{Concentration}=\beta0+\beta1(\text{Temperature})+\beta2(\text{Compound})+\beta3(\text{Mount})$
$+\beta4(\text{Angle})+\beta5(\text{Angle}^2)+\alpha1(\text{Compound*Angle})+\alpha2(\text{Compound*Angle}^2)$

Ho: The compounds differ only in level. ($\alpha1$ and $\alpha2=0$)

Reduced Model: $\text{Dye}=\beta0+\beta1(\text{Temperature})+\beta2(\text{Compound})+\beta3(\text{Mount})$
$+\beta4(\text{Angle})+\beta5(\text{Angle}^2)$

The extra sum of squares for a1 and a2 is given by

SS(b1,b2,b3,b4,b5,a1,a2|b0) - SS(b1,b2,b3,b4,b5|b0)
=RegressionSS(Full Model) - RegressionSS(Reduced Model)
with 7-5=2 degrees of freedom.

$F = (ESS/2)/MSE(\text{Full Model}) = (442.991-442.773)/2/.165 = 0.66 \quad p>.05$

Accept Ho: The compounds differ only in level, not in distribution over angle. ($\alpha1$ and $\alpha2=0$)

Tests For Effects of Design Variables on Dye Deposition

A second set of experimental runs was conducted to determine critical design parameters that would influence the measurement of the concentration distribution. The regression analysis approach allowed for the inclusion of the continuous meteorological variables into the analysis and better suited the continuous nature of many of the design parameters under consideration. The analysis for this section was conducted in two separate but similar methods. The first was an analysis by stepwise regression where variables were added to the regression one at a time. At each step the variable which most improved the regression was added until no variable significantly improved the regression. The advantage of this method was that it kept the total number of variables to a minimum while limiting the amount of colinearity between variables. The second analysis conducted was an analysis using dummy variables and the extra sum of squares tests. The advantage of this method was that it allowed for direct testing of specific hypotheses. Major differences in results between methods would have been a warning sign, indicating problems in this approach.

Stepwise Regression Tests for Dye Only Runs

The final regressions for all three sprayer types were significant at the .0001 level and had r-squares of .542,.583 and .757 for Low, Low Electrostatic and High volume sprayers respectively. The number of variables included ranged from 3 to 7. In all three sprayer types, there were significant differences in the mounting methods, with higher deposition on the rigid mounting. Because the Mount, Mount*Angle and Mount*Angle^2 variables were zero for the loose mounting and the Angle and Angle^2 variables were not included, the results implied that there was a curve in response for the rigid mount but not for the loose mounting. In the case of the low volume sprayer, there was no significant Mount dummy variable. The low volume sprayer without electrostatic charge appeared to be affected by fewer weather variables than the other two sprayers.

A stepwise regression was also run for all three sprayers combined with indicator variables for sprayer type included. Sprayer type by angle interaction variables were also included to allow for different distributions around angle for the different sprayer types. At the final step, the model included Relative Humidity, Mount, Mount*Angle, Mount*Angle Square and the indicator variable for High volume sprayer. The regression was highly significant ($p<.0001$) but the r-square of .522 indicated that a lot of the variability in dye deposition was unaccounted for. This model gave an indication that there are Relative Humidity, Mount, Angle and High volume sprayer effects. This model implied that there was a step increase in deposition of dye for the high volume sprayer vs. the other sprayer types and that there was a curved response over angle for the rigid mounting type. As with the individual sprayer runs, the linear and quadratic functions over angle for the loose mounting type did not significantly improve the regression. The relative humidity variable was the only weather variable included in the overall regression.

Extra Sum of Squares Regression Tests for Dye Only Runs.

The stepwise regressions provided a good screening for the determination of important variables and provided a good overall model. However, the stepwise regression was not a good tool for testing specific hypothesis of interest. The overall stepwise regression identified relative humidity as the weather variable which most improved the regression, so it was included in the regressions used for the extra sum of squares tests to help equalize the weather differences between runs. The first hypothesis test was therefore to test for differences in slope of relative humidity response between sprayer type. It should be noted that the three sprayer types are represented by two binary indicator variables because the third sprayer type is denoted by both indicators having values of 0.

The usual procedure would be to first test that all Sprayer*RH α's =0, but from the stepwise regression procedures we already knew that significantly more dye is deposited on the high volume spray runs. The first test was thus the test of the slopes between sprayer types. Highly significant differences in slope over RH were found between sprayer types. So we concluded there are significant differences in slopes of RH response between sprayer types, with the low volume electro static and the high volume sprayer having a significant negative slope and the low volume sprayer having a non significant positive slope.

The stepwise regressions have shown a quadratic distribution of dye over the four angles for the rigid mounting type, but the results were not as clear for the loose mounting type. For this reason, the next test was to see if any of the Mount α's were significantly different from 0. The full model was equivalent to fitting a separate quadratic regression of Dye on Angle for each mount type. The test of significance for all α's was significant. The sequential tests indicated that there were differences in the slope parameters overall and the quadratic parameter specifically. So we concluded that there were significant differences in response over angle between mount types. In testing of sprayer types, we had to include Mount*Angle interaction terms to reduce the variability due to the mount differences.

The main question of interest was if the distribution over angle was significantly different for the different sprayer types. The hypothesis that all α's =0 was rejected. The next step was to test for significant differences in the slope parameters to see if the differences were in level only. The null hypothesis of no slope differences was rejected. The high volume and low volume electrostatic were each tested against the remaining two sprayer types and found to be significantly different. Because of the quadratic components and the three sprayer types, it was decided to plot the estimated curves over angle for each sprayer type rather than conducting a complicated series of hypothesis tests.

ANOVA Results

As an alternative to the extra sum of squares regression analysis the sprayer data were analyzed as a Split Plot in Space and Time with Angle in place of the time measurement. The different sprayer runs were the whole plot, run in complete blocks with the six treatments on their frames within the sprayer runs. The angle from sprayer was considered to be more like a year effect because the whole experiment was really contained within the context of the angles where the measurements are taken. The different angles were not independent and produced a restriction on randomization which like year is more correlated for angles(years) which are closer in degrees(time) and less correlated for those farther apart. There were a number of areas where the ANOVA requirements were violated, but this analysis was sufficient to check the results of the extra sum of squares analysis.

The split plot in space and time ANOVA was run on Systat (Systat, Inc. Evanston, IL) using type III sums of squares and with correction for 4 missing data points. With four missing cells and potential violations of ANOVA assumptions the p-values should not be taken as exact. The violation of the assumptions tended to make the p-values smaller than the actual p-values. The lack of significance on the Treatment by Sprayer and Treatment by Sprayer by Angle interactions was important because it showed that the six mounting/diameter combinations, while differing in level, did not have significant interactions with sprayer type or angle and sprayer type which indicated that any of the six combinations will be equivalent for sprayer comparison. The Sprayer by Angle interaction plot showed that the concentrations over angle changed in a much smoother manner for the high volume sprayer than either of the low volume sprayers. The two low volume sprayers had a more peaked distribution with higher concentrations at Angle 2 and lower concentrations at the top and the bottom. The means plot of the Treatment by Angle interaction showed that the dye concentrations were much higher for the three rigid mount treatments at Angle 2,3 and 4. The concentrations were more variable for the rigid mounting between diameters. The 9.0cm size appeared to have lower concentrations, but with the current data set the results are not conclusive.

Conclusions

No significant differences in distribution of dye and captan over angle were found. Significant differences in level were found with the concentration significantly higher for the captan, but the regression over angle was not significantly different for the two compounds. Significant differences in level of dye and captan were found between loose and rigid mounting types, but no significant difference in regression over angle between mounting types was found. Thus the dye did have the same concentration distribution over angle, differing by a constant.

The ANOVA and extra sum of squares tests both showed significant differences in distribution over angle for the different sprayer types. The high volume sprayer had a more even distribution of concentrations over angle, while the two low volume runs had much lower concentrations at the low angle and lower concentrations at the two highest angles. The stepwise regression approach implied that there was no curve in concentration over angle for the loose mounting, but this result was not backed up by the extra sum of squares or the ANOVA. The extra sum of squares tests showed differences in distribution over angle for the loose and rigid mountings with a larger curve over angle for the rigid mounting type. The ANOVA showed a significant Treatment by Angle interaction which appeared to be primarily due to the mounting. Target diameter did not appear to be a significant factor in dye concentration in any of the analysis methods.

There are significant correlation's between several of the weather variables and the amount of dye deposited. Relative humidity was the best weather variable overall in the experiments performed here, with a significant negative correlation with dye concentration for the high volume sprayer and the low volume electrostatic sprayer. To explore the effect of weather on the sprayers, additional experiments would be required with a larger number of spray runs over the range of weather conditions.

<u>Major Points</u>

- Dye and Captan differed in level but not in distribution over angle.
- The high volume sprayer had significantly higher concentrations of dye deposited.
- The high volume sprayer had higher concentrations of dye at the low and high angles, while having slightly less than the electrostatically charged sprayer at the second angle.
- The loose mounting had lower concentrations deposited at all angles.
- The loose mounting had a more even distribution of dye concentrations over angle.
- There was no significant interaction of treatment with sprayer type.

D: Analysis Results

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye μg/cm²
4	low, elec	1	rigid	1	7	0.5037
4	low, elec	1	rigid	2	7	0.8848
4	low, elec	1	rigid	3	7	0.379
4	low, elec	1	rigid	4	7	0.2002
4	low, elec	2	rigid	1	5.5	0.6043
4	low, elec	2	rigid	2	5.5	1.0703
4	low, elec	2	rigid	3	5.5	0.6077
4	low, elec	2	rigid	4	5.5	0.3133
4	low, elec	3	loose	1	7	0.3278
4	low, elec	3	loose	2	7	0.5929
4	low, elec	3	loose	3	7	0.309
4	low, elec	3	loose	4	7	0.0913
4	low, elec	4	loose	1	5.5	0.2657
4	low, elec	4	loose	2	5.5	0.3176
4	low, elec	4	loose	3	5.5	0.2525
4	low, elec	4	loose	4	5.5	0.1158
4	low, elec	5	rigid	1	9	0.4295
4	low, elec	5	rigid	2	9	0.8183
4	low, elec	5	rigid	3	9	0.4685
4	low, elec	5	rigid	4	9	0.2405
4	low, elec	6	loose	1	9	0.3064
4	low, elec	6	loose	2	9	0.5467
4	low, elec	6	loose	3	9	0.2872
4	low, elec	6	loose	4	9	0.1671
5	high	1	loose	1	7	0.4848
5	high	1	loose	2	7	0.6499
5	high	1	loose	3	7	0.7558
5	high	1	loose	4	7	0.6171
5	high	2	rigid	1	9	0.8494
5	high	2	rigid	2	9	1.2743
5	high	2	rigid	3	9	1.4098
5	high	2	rigid	4	9	1.0942
5	high	3	loose	1	9	0.5734
5	high	3	loose	2	9	0.7476
5	high	3	loose	3	9	0.8561
5	high	3	loose	4	9	0.5709
5	high	4	rigid	1	7	0.7613
5	high	4	rigid	2	7	0.9795
5	high	4	rigid	3	7	1.3803
5	high	4	rigid	4	7	1.2362
5	high	5	loose	1	5.5	0.3765
5	high	5	loose	2	5.5	0.6369
5	high	5	loose	3	5.5	0.688
5	high	5	loose	4	5.5	0.688
5	high	6	rigid	1	5.5	0.6698
5	high	6	rigid	2	5.5	1.1236
5	high	6	rigid	3	5.5	1.4955
5	high	6	rigid	4	5.5	1.2486

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye $\mu g/cm^2$
6	low	1	loose	1	7	0.1434
6	low	1	loose	2	7	0.4781
6	low	1	loose	3	7	0.5105
6	low	1	loose	4	7	0.3283
6	low	2	rigid	1	9	0.1276
6	low	2	rigid	2	9	1.2529
6	low	2	rigid	3	9	0.963
6	low	2	rigid	4	9	1.0145
6	low	3	rigid	1	5.5	0.0189
6	low	3	rigid	2	5.5	1.6134
6	low	3	rigid	3	5.5	1.1714
6	low	3	rigid	4	5.5	1.1868
6	low	4	loose	1	9	0.0344
6	low	4	loose	2	9	0.7892
6	low	4	loose	3	9	0.5835
6	low	4	loose	4	9	0.4664
6	low	5	loose	1	5.5	0.0916
6	low	5	loose	2	5.5	0.4542
6	low	5	loose	3	5.5	0.4842
6	low	5	loose	4	5.5	0.4811
6	low	6	rigid	1	7	0.0301
6	low	6	rigid	2	7	0.799
6	low	6	rigid	3	7	1.2204
6	low	6	rigid	4	7	1.1439
7	high	1	rigid	1	7	1.3923
7	high	1	rigid	2	7	1.7428
7	high	1	rigid	3	7	1.7806
7	high	1	rigid	4	7	1.541
7	high	2	loose	1	9	N/A
7	high	2	loose	2	9	1.017
7	high	2	loose	3	9	0.9633
7	high	2	loose	4	9	0.8081
7	high	3	rigid	1	9	0.6816
7	high	3	rigid	2	9	0.975
7	high	3	rigid	3	9	0.7503
7	high	3	rigid	4	9	1.2407
7	high	4	loose	1	7	0.6496
7	high	4	loose	2	7	0.9273
7	high	4	loose	3	7	0.9297
7	high	4	loose	4	7	0.6802
7	high	5	rigid	1	5.5	1.1405
7	high	5	rigid	2	5.5	1.7198
7	high	5	rigid	3	5.5	1.9905
7	high	5	rigid	4	5.5	1.6779
7	high	6	loose	1	5.5	0.6973
7	high	6	loose	2	5.5	0.9395
7	high	6	loose	3	5.5	0.8896
7	high	6	loose	4	5.5	0.7624

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye µg/cm²
8	low	1	loose	1	9	0.3557
8	low	1	loose	2	9	1.0791
8	low	1	loose	3	9	0.9001
8	low	1	loose	4	9	0.6981
8	low	2	rigid	1	5.5	0.2069
8	low	2	rigid	2	5.5	1.9603
8	low	2	rigid	3	5.5	1.7918
8	low	2	rigid	4	5.5	1.3731
8	low	3	rigid	1	7	0.1276
8	low	3	rigid	2	7	1.9562
8	low	3	rigid	3	7	1.6228
8	low	3	rigid	4	7	1.54
8	low	4	rigid	1	9	0.149
8	low	4	rigid	2	9	1.9126
8	low	4	rigid	3	9	1.624
8	low	4	rigid	4	9	1.3652
8	low	5	loose	1	7	0.2397
8	low	5	loose	2	7	1.19
8	low	5	loose	3	7	0.8821
8	low	5	loose	4	7	0.5328
8	low	6	loose	1	5.5	0.1657
8	low	6	loose	2	5.5	0.5213
8	low	6	loose	3	5.5	0.7144
8	low	6	loose	4	5.5	0.4459
9	low, elec	1	loose	1	9	0.5577
9	low, elec	1	loose	2	9	0.6673
9	low, elec	1	loose	3	9	0.3852
9	low, elec	1	loose	4	9	0.5327
9	low, elec	2	loose	1	7	0.6475
9	low, elec	2	loose	2	7	1.4561
9	low, elec	2	loose	3	7	0.7519
9	low, elec	2	loose	4	7	0.8089
9	low, elec	3	rigid	1	9	0.5299
9	low, elec	3	rigid	2	9	2.2008
9	low, elec	3	rigid	3	9	1.2263
9	low, elec	3	rigid	4	9	1.5656
9	low, elec	4	rigid	1	7	0.6481
9	low, elec	4	rigid	2	7	2.0356
9	low, elec	4	rigid	3	7	2.1052
9	low, elec	4	rigid	4	7	1.7759
9	low, elec	5	rigid	1	5.5	0.679
9	low, elec	5	rigid	2	5.5	1.7204
9	low, elec	5	rigid	3	5.5	2.6204
9	low, elec	5	rigid	4	5.5	1.8115
9	low, elec	6	loose	1	5.5	0.2993
9	low, elec	6	loose	2	5.5	1.048
9	low, elec	6	loose	3	5.5	0.7252
9	low, elec	6	loose	4	5.5	0.5393

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye µg/cm²
10	low	1	rigid	1	5.5	0.4252
10	low	1	rigid	2	5.5	1.8439
10	low	1	rigid	3	5.5	0.9099
10	low	1	rigid	4	5.5	0.8941
10	low	2	loose	1	5.5	0.2656
10	low	2	loose	2	5.5	0.9551
10	low	2	loose	3	5.5	0.4635
10	low	2	loose	4	5.5	0.462
10	low	3	rigid	1	9	0.3368
10	low	3	rigid	2	9	1.9828
10	low	3	rigid	3	9	0.8977
10	low	3	rigid	4	9	1.3546
10	low	4	rigid	1	7	0.4984
10	low	4	rigid	2	7	1.9249
10	low	4	rigid	3	7	0.8864
10	low	4	rigid	4	7	1.2743
10	low	5	loose	1	9	0.1245
10	low	5	loose	2	9	1.0894
10	low	5	loose	3	9	0.5333
10	low	5	loose	4	9	0.7805
10	low	6	loose	1	7	0.1563
10	low	6	loose	2	7	1.3429
10	low	6	loose	3	7	0.6408
10	low	6	loose	4	7	0.7076
11	low, elec	1	rigid	1	9	0.1728
11	low, elec	1	rigid	2	9	1.6707
11	low, elec	1	rigid	3	9	1.1673
11	low, elec	1	rigid	4	9	1.2643
11	low, elec	2	rigid	1	7	0.1509
11	low, elec	2	rigid	2	7	1.4296
11	low, elec	2	rigid	3	7	1.2798
11	low, elec	2	rigid	4	7	1.042
11	low, elec	3	loose	1	9	0.1705
11	low, elec	3	loose	2	9	1.1753
11	low, elec	3	loose	3	9	0.9601
11	low, elec	3	loose	4	9	0.7043
11	low, elec	4	loose	1	7	0.1098
11	low, elec	4	loose	2	7	1.0846
11	low, elec	4	loose	3	7	0.8061
11	low, elec	4	loose	4	7	0.6048
11	low, elec	5	loose	1	5.5	0.1647
11	low, elec	5	loose	2	5.5	1.11
11	low, elec	5	loose	3	5.5	0.9101
11	low, elec	5	loose	4	5.5	0.4937
11	low, elec	6	rigid	1	5.5	0.2549
11	low, elec	6	rigid	2	5.5	1.6459
11	low, elec	6	rigid	3	5.5	2.2837
11	low, elec	6	rigid	4	5.5	1.0268

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye $\mu g/cm^2$
12	high	1	rigid	1	5.5	1.2786
12	high	1	rigid	2	5.5	1.7637
12	high	1	rigid	3	5.5	2.2388
12	high	1	rigid	4	5.5	1.7125
12	high	2	loose	1	7	0.7077
12	high	2	loose	2	7	1.0625
12	high	2	loose	3	7	1.0855
12	high	2	loose	4	7	0.7585
12	high	3	rigid	1	7	1.6826
12	high	3	rigid	2	7	2.1349
12	high	3	rigid	3	7	2.2069
12	high	3	rigid	4	7	1.8624
12	high	4	loose	1	5.5	0.9747
12	high	4	loose	2	5.5	1.1164
12	high	4	loose	3	5.5	1.1417
12	high	4	loose	4	5.5	1.0057
12	high	5	loose	1	9	1.0753
12	high	5	loose	2	9	1.2255
12	high	5	loose	3	9	1.2668
12	high	5	loose	4	9	1.1349
12	high	6	rigid	1	9	N/A
12	high	6	rigid	2	9	N/A
12	high	6	rigid	3	9	N/A
12	high	6	rigid	4	9	1.8245
13	low, elec	1	rigid	1	5.5	0.7846
13	low, elec	1	rigid	2	5.5	2.4212
13	low, elec	1	rigid	3	5.5	1.5938
13	low, elec	1	rigid	4	5.5	1.8008
13	low, elec	2	loose	1	9	0.3504
13	low, elec	2	loose	2	9	1.2781
13	low, elec	2	loose	3	9	0.9439
13	low, elec	2	loose	4	9	0.7118
13	low, elec	3	loose	1	5.5	0.458
13	low, elec	3	loose	2	5.5	1.6778
13	low, elec	3	loose	3	5.5	0.9454
13	low, elec	3	loose	4	5.5	0.9065
13	low, elec	4	rigid	1	9	0.5125
13	low, elec	4	rigid	2	9	1.7578
13	low, elec	4	rigid	3	9	1.1666
13	low, elec	4	rigid	4	9	1.0286
13	low, elec	5	rigid	1	7	0.5443
13	low, elec	5	rigid	2	7	2.3525
13	low, elec	5	rigid	3	7	1.4188
13	low, elec	5	rigid	4	7	1.0905
13	low, elec	6	loose	1	7	0.5254
13	low, elec	6	loose	2	7	1.1657
13	low, elec	6	loose	3	7	0.6602
13	low, elec	6	loose	4	7	0.5857

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye µg/cm²
14	low	1	rigid	1	7	0.0301
14	low	1	rigid	2	7	1.0509
14	low	1	rigid	3	7	0.9542
14	low	1	rigid	4	7	1.0233
14	low	2	loose	1	9	0.0246
14	low	2	loose	2	9	0.6342
14	low	2	loose	3	9	0.5216
14	low	2	loose	4	9	0.4467
14	low	3	loose	1	5.5	0.0044
14	low	3	loose	2	5.5	0.6761
14	low	3	loose	3	5.5	0.5874
14	low	3	loose	4	5.5	0.4478
14	low	4	loose	1	7	0.0225
14	low	4	loose	2	7	0.492
14	low	4	loose	3	7	0.5832
14	low	4	loose	4	7	0.4888
14	low	5	rigid	1	9	0.1553
14	low	5	rigid	2	9	1.4076
14	low	5	rigid	3	9	1.1149
14	low	5	rigid	4	9	0.9672
14	low	6	rigid	1	5.5	0.1174
14	low	6	rigid	2	5.5	1.0862
14	low	6	rigid	3	5.5	1.2479
14	low	6	rigid	4	5.5	0.8421
15	high	1	loose	1	9	0.7171
15	high	1	loose	2	9	0.8021
15	high	1	loose	3	9	0.7593
15	high	1	loose	4	9	0.7399
15	high	2	rigid	1	9	1.088
15	high	2	rigid	2	9	1.2786
15	high	2	rigid	3	9	1.0996
15	high	2	rigid	4	9	1.1622
15	high	3	rigid	1	5.5	1.0512
15	high	3	rigid	2	5.5	1.3782
15	high	3	rigid	3	5.5	1.3859
15	high	3	rigid	4	5.5	1.4976
15	high	4	loose	1	7	0.7206
15	high	4	loose	2	7	0.8515
15	high	4	loose	3	7	0.8982
15	high	4	loose	4	7	0.7314
15	high	5	rigid	1	7	1.1536
15	high	5	rigid	2	7	1.3571
15	high	5	rigid	3	7	1.3458
15	high	5	rigid	4	7	1.1392
15	high	6	loose	1	5.5	0.7765
15	high	6	loose	2	5.5	1.0593
15	high	6	loose	3	5.5	1.0295
15	high	6	loose	4	5.5	0.8077

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye µg/cm²
16	low, elec	1	loose	1	7	0.0731
16	low, elec	1	loose	2	7	0.6024
16	low, elec	1	loose	3	7	0.2472
16	low, elec	1	loose	4	7	0.3118
16	low, elec	2	loose	1	5.5	0.1282
16	low, elec	2	loose	2	5.5	0.8145
16	low, elec	2	loose	3	5.5	0.3611
16	low, elec	2	loose	4	5.5	0.4071
16	low, elec	3	rigid	1	7	0.1866
16	low, elec	3	rigid	2	7	1.2564
16	low, elec	3	rigid	3	7	0.7423
16	low, elec	3	rigid	4	7	0.7712
16	low, elec	4	rigid	1	5.5	0.1734
16	low, elec	4	rigid	2	5.5	1.5468
16	low, elec	4	rigid	3	5.5	0.7647
16	low, elec	4	rigid	4	5.5	0.9986
16	low, elec	5	loose	1	9	0.066
16	low, elec	5	loose	2	9	0.8299
16	low, elec	5	loose	3	9	0.433
16	low, elec	5	loose	4	9	0.556
16	low, elec	6	rigid	1	9	0.2526
16	low, elec	6	rigid	2	9	1.5177
16	low, elec	6	rigid	3	9	0.6527
16	low, elec	6	rigid	4	9	0.8126
17	low	1	rigid	1	9	0.0825
17	low	1	rigid	2	9	1.2837
17	low	1	rigid	3	9	0.6792
17	low	1	rigid	4	9	0.8479
17	low	2	rigid	1	7	0.117
17	low	2	rigid	2	7	1.2737
17	low	2	rigid	3	7	0.7033
17	low	2	rigid	4	7	0.7988
17	low	3	loose	1	7	0.042
17	low	3	loose	2	7	0.6128
17	low	3	loose	3	7	0.2963
17	low	3	loose	4	7	0.3208
17	low	4	loose	1	5.5	0.0264
17	low	4	loose	2	5.5	0.8287
17	low	4	loose	3	5.5	0.3737
17	low	4	loose	4	5.5	0.3769
17	low	5	rigid	1	5.5	0.0329
17	low	5	rigid	2	5.5	1.5688
17	low	5	rigid	3	5.5	0.9442
17	low	5	rigid	4	5.5	0.9136
17	low	6	loose	1	9	0.092
17	low	6	loose	2	9	0.8839
17	low	6	loose	3	9	0.6281
17	low	6	loose	4	9	0.4707

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye $\mu g/cm^2$
18	high	1	rigid	1	9	1.0401
18	high	1	rigid	2	9	1.3802
18	high	1	rigid	3	9	1.5871
18	high	1	rigid	4	9	1.2883
18	high	2	rigid	1	5.5	1.3061
18	high	2	rigid	2	5.5	1.9404
18	high	2	rigid	3	5.5	1.9028
18	high	2	rigid	4	5.5	1.9279
18	high	3	loose	1	5.5	0.699
18	high	3	loose	2	5.5	0.7482
18	high	3	loose	3	5.5	0.8467
18	high	3	loose	4	5.5	0.8735
18	high	4	loose	1	9	0.6629
18	high	4	loose	2	9	0.9652
18	high	4	loose	3	9	1.1849
18	high	4	loose	4	9	0.8607
18	high	5	rigid	1	7	1.1769
18	high	5	rigid	2	7	1.6866
18	high	5	rigid	3	7	2.1245
18	high	5	rigid	4	7	2.4951
18	high	6	loose	1	7	0.9041
18	high	6	loose	2	7	0.9067
18	high	6	loose	3	7	1.375
18	high	6	loose	4	7	0.9906

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye μg/cm²	Captan μg/cm²
C1	high	1	loose	1	7	N/A	N/A
C1	high	1	loose	2	7	0.3901	6.81
C1	high	1	loose	3	7	0.4479	13.12
C1	high	1	loose	4	7	0.3685	4.36
C1	high	2	rigid	1	7	0.4045	15.51
C1	high	2	rigid	2	7	0.9524	24.13
C1	high	2	rigid	3	7	0.8265	25.99
C1	high	2	rigid	4	7	0.7105	26.36
C1	high	3	rigid	1	7	0.3885	4.84
C1	high	3	rigid	2	7	0.9180	27.84
C1	high	3	rigid	3	7	0.8115	25.61
C1	high	3	rigid	4	7	0.8132	23.39
C1	high	4	loose	1	7	0.2732	3.84
C1	high	4	loose	2	7	0.3752	4.80
C1	high	4	loose	3	7	0.4081	5.14
C1	high	4	loose	4	7	0.2434	3.50
C1	high	5	loose	1	7	0.2467	3.02
C1	high	5	loose	2	7	0.3892	4.29
C1	high	5	loose	3	7	0.2662	5.14
C1	high	5	loose	4	7	0.4430	4.57
C1	high	6	rigid	1	7	0.7636	10.15
C1	high	6	rigid	2	7	0.6399	12.41
C1	high	6	rigid	3	7	0.8236	14.56
C1	high	6	rigid	4	7	1.1345	15.05
C2	high	1	loose	1	7	0.5783	8.46
C2	high	1	loose	2	7	0.8465	10.48
C2	high	1	loose	3	7	0.8538	9.61
C2	high	1	loose	4	7	0.5921	9.17
C2	high	2	loose	1	7	0.6448	7.19
C2	high	2	loose	2	7	0.8519	9.61
C2	high	2	loose	3	7	0.7714	12.88
C2	high	2	loose	4	7	0.4946	7.64
C2	high	3	rigid	1	7	1.3931	15.39
C2	high	3	rigid	2	7	0.8620	19.00
C2	high	3	rigid	3	7	1.1063	21.32
C2	high	3	rigid	4	7	0.8411	17.25
C2	high	4	loose	1	7	0.6595	12.58
C2	high	4	loose	2	7	0.7731	13.75
C2	high	4	loose	3	7	0.9687	15.75
C2	high	4	loose	4	7	0.5590	11.41
C2	high	5	rigid	1	7	0.8421	14.67
C2	high	5	rigid	2	7	0.9881	17.01
C2	high	5	rigid	3	7	1.0143	16.13
C2	high	5	rigid	4	7	1.7376	22.32
C2	high	6	rigid	1	7	0.8237	10.65
C2	high	6	rigid	2	7	0.9291	13.48
C2	high	6	rigid	3	7	1.1648	14.80
C2	high	6	rigid	4	7	1.1521	13.56

Run	Sprayer	Frame	Mount	Angle	Diameter cm	Dye µg/cm²	Captan µg/cm²
C3	high	1	rigid	1	7	0.8766	14.72
C3	high	1	rigid	2	7	0.6746	17.28
C3	high	1	rigid	3	7	1.2745	23.84
C3	high	1	rigid	4	7	0.6056	16.41
C3	high	2	rigid	1	7	0.7407	12.89
C3	high	2	rigid	2	7	0.9365	19.84
C3	high	2	rigid	3	7	1.4866	21.88
C3	high	2	rigid	4	7	1.4140	23.44
C3	high	3	loose	1	7	0.8863	12.31
C3	high	3	loose	2	7	0.7011	13.48
C3	high	3	loose	3	7	0.8899	12.89
C3	high	3	loose	4	7	0.6855	9.38
C3	high	4	loose	1	7	0.5759	8.62
C3	high	4	loose	2	7	0.8830	10.94
C3	high	4	loose	3	7	0.4613	6.92
C3	high	4	loose	4	7	0.6069	6.32
C3	high	5	rigid	1	7	0.5701	13.09
C3	high	5	rigid	2	7	1.7994	17.13
C3	high	5	rigid	3	7	1.7338	23.53
C3	high	5	rigid	4	7	1.1769	15.25
C3	high	6	loose	1	7	0.3806	8.00
C3	high	6	loose	2	7	0.6939	10.18
C3	high	6	loose	3	7	0.6379	9.43
C3	high	6	loose	4	7	0.5945	7.91
C4	high	1	rigid	1	7	0.2551	12.64
C4	high	1	rigid	2	7	0.5782	27.25
C4	high	1	rigid	3	7	0.4274	25.27
C4	high	1	rigid	4	7	0.7712	22.90
C4	high	2	loose	1	7	0.2998	13.43
C4	high	2	loose	2	7	0.3001	12.73
C4	high	2	loose	3	7	0.3520	18.56
C4	high	2	loose	4	7	0.2483	8.35
C4	high	3	rigid	1	7	0.6625	25.67
C4	high	3	rigid	2	7	1.0947	46.60
C4	high	3	rigid	3	7	0.7487	44.08
C4	high	3	rigid	4	7	0.7842	28.43
C4	high	4	rigid	1	7	0.5818	9.28
C4	high	4	rigid	2	7	0.8111	12.92
C4	high	4	rigid	3	7	N/A	30.89
C4	high	4	rigid	4	7	N/A	24.04
C4	high	5	loose	1	7	0.2529	3.71
C4	high	5	loose	2	7	N/A	10.74
C4	high	5	loose	3	7	0.3689	14.34
C4	high	5	loose	4	7	0.3695	14.02
C4	high	6	loose	1	7	0.1907	2.69
C4	high	6	loose	2	7	0.2535	6.76
C4	high	6	loose	3	7	0.2637	12.44
C4	high	6	loose	4	7	0.2768	8.49

E: Meteorological data

Run	Sprayer	Wind mph	Wind deg	Temp (F)	RH %
4	low, elec	4	190	63	83
5	high	1	290	52	94
6	low	5	310	62	80
7	high	4	160	54	95
8	low	3	280	60	83
9	low, elec	5	180	73	56
10	low	0	N/A	50	94
11	low, elec	0	N/A	57	83
12	high	4	180	72	60
13	low, elec	0	N/A	58	86
14	low	3	300	59	100
15	high	5	350	62	97
16	low, elec	0	N/A	57	82
17	low	0	N/A	68	65
18	high	3	20	79	50
C1	high	4	150	47	72
C2	high	5	340	49	85
C3	high	3	80	55	76
C4	high	2	160	59	73